

Quenching of Impurity Spins at Cu/CuO Interfaces: An Antiferromagnetic Proximity Effect

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It is observed that the magnetoconductance of bilayer films of copper (Cu) and copper monoxide (CuO) has distinct features compared of that of Cu films on conventional band insulator substrates. We analyze the data above 2 K by the theory of weak antilocalization in two-dimensional metals and suggest that spin-flip scatterings by magnetic impurities inside Cu are suppressed in Cu/CuO samples. Plausibly the results imply a proximity effect of antiferromagnetism inside the Cu layer, which can be understood in the framework of Ruderman-Kittel-Kasuya-Yoshida (RKKY) interactions. The data below 1 K, which exhibit slow relaxation reminiscent of spin glass, are consistent with this interpretation.

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As the technology to synthesize high-quality thin films and thin film interfaces steadily improves, there has been an extensive search for novel physical properties in thin film heterostructures in the condensed matter physics community. In fact, numerous heterostructure interfaces have been found to exhibit unique phenomena that are not present in bulk materials. Some prominent examples include the exchange bias effects in antiferromagnet/ferromagnet interfaces [1], high-mobility two-dimensional electron gases in semiconductor and complex oxide heterostructures [2, 3], and various proximity effects. The proximity effect at solid state interfaces can be defined as a mutual induction of certain physical properties from one material into an adjacent one across their interface. The most famous example is that of superconductivity, where superconducting pairs are induced in a neighboring normal metal while normal electrons in the metal permeate the superconductor [4, 5].

At the interfaces between a metal and a non-superconducting material, especially an insulator, one might naively expect no proximity effect besides a simple transfer of charges and development of a Schottky barrier. In this paper, however, we present evidence for a new proximity effect that arises between a normal metal and an antiferromagnetic (AF) charge-transfer insulator. Specifically, we show evidence for the creation of AF spin ordering in a normal metal due to the proximity effect through spin-spin interactions with an AF charge transfer insulator. The existence of such a proximity effect has been anticipated theoretically [6]. The heterostructure of a copper (Cu) thin film and a copper monoxide (CuO) thin film was synthesized as a potential model system for such a proximity effect [7]. This Cu/CuO bilayer exhibits distinct features in magnetotransport compared to a Cu thin film on a conventional band insulator substrate. The magnetoconductance of both films above 2 K can be analyzed by the theory of weak antilocalization and indicates the quenching of spin-flip scatterings by

magnetic impurities inside the Cu in proximity to CuO. This non-local effect in magnetotransport by an AF insulator can be naturally interpreted as a consequence of AF spin ordering induced in the Cu.

Smooth thin Cu/CuO bilayer films were synthesized on magnesium oxide (MgO) substrates. We first cleaned a MgO (001) substrate and deposited a 21 nm CuO film as described in the supplementary material [8]. After the deposition of CuO, the sample was cooled down to room temperatures under plasma-excited atomic oxygen flux. We then turned off the atomic oxygen flux and deposited a 3 nm Cu film in vacuum by electron beam evaporation. As a comparison, we also synthesized 3 nm Cu films using the same Cu source on several different band insulator substrates (MgO, Al₂O₃, Si), which we collectively call Cu/BI films because all the films behaved in the similar way in the transport measurements. The transport properties were measured with a Quantum Design Physical Property Measurement System.

Figs. 1 (a) and (b) represent the sheet resistance of Cu/CuO and Cu/MgO films, respectively, as functions of temperature. While the resistance of both films above 50 K increases with temperature as expected for a simple metal, both samples have a minimum in the sheet resistance about 50 K. In order to further examine the transport properties of the two films, we show in Figs. 2 (a) and (b) the sheet conductance as a function of external magnetic field H perpendicular to the films at different temperatures between 2 K and 10 K. In both samples, the magnetoconductance is negative at fields lower than ~ 0.4 T and positive at higher fields, which become more evident at lower temperatures.

These transport properties in two-dimensional metallic systems like Cu are well known and were extensively examined since the late 1970s and attributed to a weak localization/antilocalization effect [6, 8–12]. In fact, since CuO and band insulators have much higher resistance at these temperatures than Cu, the current must predomi-

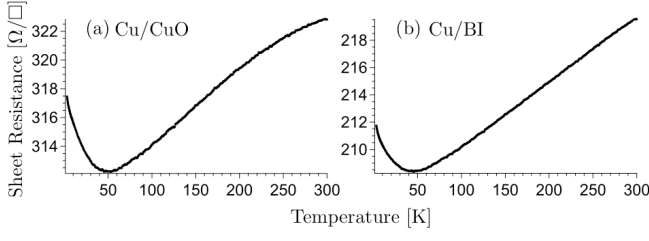


FIG. 1. Temperature dependence of sheet resistance of (a) the Cu/CuO and (b) the Cu/MgO film. The deviation from the straight line above 200 K in (a) is due to the resistance of CuO.

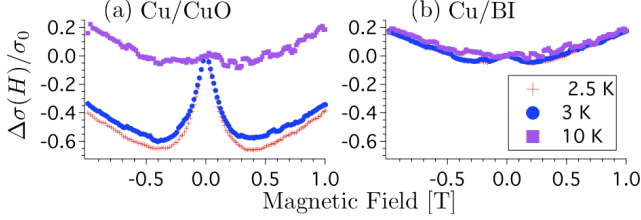


FIG. 2. Normalized magnetoconductance at 2.5 K, 3 K, and 10 K of (a) the Cu/CuO and (b) the Cu/MgO film. $\Delta\sigma(H)$ is the difference in sheet conductance between the value under a magnetic field H and the zero-field value, while $\sigma_0 \equiv e^2/\pi h \simeq 1.23 \times 10^{-5}$ S is a constant for the normalization.

nantly flow inside the Cu. This consideration, together with the fact that both Cu films were deposited from the identical, fully melted Cu source using the same e-beam system, reasonably suggests that there should be no big difference between the transport properties of Cu/CuO and Cu/Bi films. However, Fig. 2 also shows a large difference in detailed shapes of the curves: The negative component of the magnetoconductance at magnetic fields lower than 0.4 T is much more prominent in the Cu/CuO film than in the Cu/MgO film. This is the essential experimental finding in this paper.

In order to examine the origin of this difference, we analyze the data by fitting the magnetoconductance curves to the theoretical equation for the weak antilocalization effect [9, 11, 14]:

$$\frac{\Delta\sigma(H)}{\sigma_0} = -\frac{3}{2} \left\{ \ln \frac{\frac{4}{3}H_1 + H_2}{H} - \psi\left(\frac{1}{2} + \frac{\frac{4}{3}H_1 + H_2}{H}\right) \right\} + \frac{1}{2} \left\{ \ln \frac{H_2}{H} - \psi\left(\frac{1}{2} + \frac{H_2}{H}\right) \right\}$$

In the equation above, $\Delta\sigma(H)$ is the difference in sheet conductance between the value under a magnetic field H and the zero-field value. There are two fitting parameters $H_1 \equiv H_{so} - H_s$ and $H_2 \equiv H_i + 2H_s$, where $H_i \equiv \hbar/4eD\tau_i$ is the effective field proportional to the inelastic scattering rate $1/\tau_i$, $H_s \equiv \hbar/4eD\tau_s$ is proportional to the spin-flip scattering rate $1/\tau_s$, and $H_{so} \equiv \hbar/4eD\tau_{so}$ is proportional to the spin-orbit scattering rate $1/\tau_{so}$.

$\sigma_0 \equiv e^2/\pi h \simeq 1.23 \times 10^{-5}$ S is a constant with the unit of conductance, D is the diffusion constant for electron motion inside Cu films, and ψ is the digamma function. We emphasize that this formula and its relatives have been successfully applied to many metallic thin films [10, 11] as well as two-dimensional electron gas systems [15, 16], which supports the reliability of our analysis.

We examine the temperature dependence of the different scattering rates by fitting the experimental curve at each temperature by the theoretical equation. Figure 3 (a) represents the temperature dependence of H_1 , which is related to the spin-orbit and spin-flip scattering rates. The two films have similar values in H_1 , which do not seem to have significant temperature dependence. Since both the spin-orbit scattering and the spin-flip scattering are expected to be temperature independent [17], the experimental results that H_1 does not exhibit large temperature dependence assure the validity of our analysis.

On the other hand, the temperature dependence of H_2 , as shown in Fig. 3 (b), demonstrates the clear difference in transport properties between Cu/CuO and Cu/MgO films. While at temperatures higher than 10 K both films show similar decrease of H_2 as temperature decreases, the decrease of H_2 of the Cu/MgO becomes much slower than that of the Cu/CuO film below 10 K. In fact, the saturation of the decrease in H_2 in thin metallic films including Cu has been observed in previous studies by other researchers [10, 11]. Since H_2 is a weighted sum of inelastic and spin-flip scattering rates, the saturation has been attributed to the presence of small amount of magnetic impurities which contributes to the spin-flip scattering. It is therefore natural to speculate that our Cu films also have magnetic impurities. In fact, using the secondary ion mass spectrometry [8], we observed several trace magnetic impurities (Cr, Fe, Mn, Ni, and Co) in a much thicker Cu film deposited from the same Cu source. What is unexpected, however, is that, even though we deposited Cu on CuO from the identical Cu source, we do not see the saturation of the decrease of H_2 in the Cu/CuO film.

We further observe that H_2 of the Cu/CuO film between 2 K and 4 K is roughly proportional to temperature, though this is not very conclusive due to the narrow range of the measurements. Since theoretically the inelastic scattering rate by electron-electron scattering in disordered metals is also expected to roughly scale as $\sim T^1$ [18, 19], this observation implies that H_2 in this sample is dominated not by the spin-flip scattering but by the inelastic scattering.

By plotting H_2 as a function of temperature in a linear scale (Fig. 3 (d)) and linearly extrapolating each curve down to 0K, the spin-flip scattering time τ_s of each sample can be estimated. We can then use the value of H_1 (Fig. 3 (c)) to obtain the spin-orbit scattering time. The results of the analysis are summarized in Table I for reference. Table I clearly demonstrates that τ_s of the

TABLE I. Summary of the magnetoconductance analysis on our films. d and R_s represent the thickness and the minimum sheet resistance, respectively. The thickness d is estimated from dR_s/dT (the slope of Fig. 1) between 150 K and 200 K. For the discussion on why d is smaller than the nominal thickness (3 nm), please refer to the supplementary material [8]. Spin-orbit, inelastic, and spin-flip scattering times are evaluated using the data in Fig. 3. The error range of each value is simply estimated by the standard error of the linear regression. For the calculation of the scattering times, we adopted the following parameters for Cu: electron mass = 9.1×10^{-31} kg; fermi velocity = 1.6×10^6 m/s; and carrier density = 8.5×10^{28} m $^{-3}$.

	d [nm]	R_s [Ω/\square]	τ_{so} [10^{-12} s]	$\tau_i T$ [10^{-11} s·K]	τ_s [10^{-12} s]
Cu/CuO	1.3	312	1.4	2.7	$(7.1 \pm 0.4) \times 10^1$
Cu/MgO	1.4	208	1.3	2.7 ± 1.5	4.6 ± 0.8
Cu/Al $_2$ O $_3$	1.5	138	2.1 ± 0.3	3.3 ± 2.8	6.1 ± 1.6

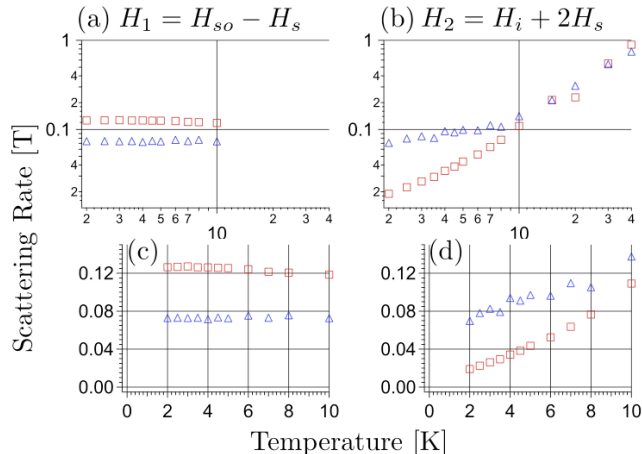


FIG. 3. Temperature dependence of (a) H_1 in a log scale, (b) H_2 in a log scale, (c) H_1 in a linear scale, and (d) H_2 in a linear scale. In each figure, squares represent the Cu/CuO film, while triangles represent the Cu/MgO film.

Cu/CuO film is anomalously long compared to that of the Cu/BI films. On the other hand, the fact that τ_{so} of each film agrees well further confirms the validity of our analysis. We note that, depending on the thickness of the films, the spin-orbit scattering times of copper films in the literature roughly range from 10^{-12} to 10^{-11} s [6, 12], which is consistent with our results. Table I also shows the results of analysis in a slightly thicker and less disordered Cu/Al $_2$ O $_3$ film for comparison. Although the data are more noisy, τ_s of this film is very similar to that of the Cu/MgO film. This observation safely excludes the possibility that the magnetic impurities originate from a surface of any particular BI substrate.

All the experimental results presented so far suggest a single story: while both Cu films contain magnetic impurities, the spin-flip scattering by the magnetic impurities in the Cu/CuO film is suppressed due to the adjacent CuO layer. We can understand this phenomenon in the following way. Since the spins in CuO are antiferromagnetically aligned below its Néel temperature (~ 200 K) as depicted in Fig. 4, each nearly-free electron in the Cu is spin-polarized by the superposition of RKKY in-

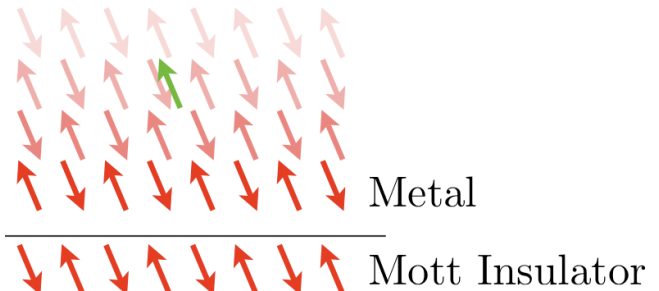


FIG. 4. Schematic picture of the proximity effect of antiferromagnetism implied by our experimental results. The arrows represent electron spins. This figure serves as an intuitive understanding of how the electron spins inside the metal are polarized by the surface spins of the antiferromagnetic insulator, and how the spin of each magnetic impurity, which is represented as a green arrow, is quenched due to the interactions with neighboring spins in the metal. Note that the actual spatial configuration of spin density induced in the Cu is probably much more complicated than depicted in this figure due to the low symmetry of the surface spin configuration of the CuO.

teractions [21–23] from all the spins on the surface layer of the CuO [20], which results in an AF alignment of spins inside the Cu. In this situation, the spin of each magnetic impurity feels the spin-polarization of mobile electrons around it through a conventional exchange interaction. Such an interaction with polarized spins naturally creates an energy cost for the spin-flip process of the magnetic impurity. When the temperature is lower than this energy cost, the spin-flip scattering by the magnetic impurity is exponentially suppressed.

The two copper films measured in a dilution refrigerator exhibit another characteristic feature below about 1 K, a hysteresis of magnetoconductance. While the data are presented elsewhere, we here note that the presence of the hysteresis implies the extended relaxation time in spin glass [1] and is probably due to RKKY interactions between magnetic impurity spins inside the Cu films [24]. We emphasize that the two copper films with different substrates have similar magnitudes of hysteresis. This observation suggests that the type of magnetic impurities and their concentration are similar in both films, and is

consistent with our interpretation of the results above 2 K explained above.

In conclusion, through the magnetotransport study above 2 K, spin-flip scattering is found to be suppressed in Cu/CuO films, whereas the results in Cu/BI films clearly indicate the presence of magnetic impurities. We propose that the observations are indirect evidence of the proximity effect of antiferromagnetism in the metal.

Even though the effect presented in this paper is subtle, it might find some interesting applications in the future. For example, spintronics utilizes the electron's spin and magnetic moment to affect electrical transport. A common problem in this context is the undesired relaxation of spin-polarized carriers, possibly due to magnetic impurities. Therefore, our experimental results could have implications for future spintronic experiments.

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- [1] R. M. White, *Quantum theory of magnetism, third edition* (Springer, New York, 2006).
- [2] W. A. Harrison, E. A. Kraut, J. R. Waldrop, and R. W. Grant, *Physical Review B* **18**, 4402 (1978).
- [3] A. Ohtomo and H. Y. Hwang, *Nature* **427**, 423 (2004).
- [4] W. L. McMillan, *Physical Review* **175**, 537 (1968).
- [5] A. I. Buzdin, *Reviews of Modern Physics* **77**, 935 (2005).
- [6] Recently there have been explicit theoretical calculations of the proximity effect of antiferromagnetism in a metal/AF Mott insulator bilayer [25] and in related systems realized by ultracold atoms [26], though we describe the similar physics from the point of view of RKKY interactions in Fig. 4.
- [7] Our model system is reminiscent of the heterostructures of underdoped and overdoped cuprates, which have recently been demonstrated to have an enhanced superconducting transition temperature [27, 28]. We speculate that such enhancement of transition temperatures, as originally proposed theoretically [29, 30], might involve a physics similar to the phenomenon presented in this letter if the superconductivity in cuprates is due to antiferromagnetic spin fluctuations [29].
- [8] See the supplementary information attached below for details about film synthesis, characterizations, and interpretations of our data.
- [9] S. Maekawa and H. Fukuyama, *Journal of the Physical Society of Japan* **50**, 2516 (1981).
- [10] D. Abraham and R. Rosenbaum, *Physical Review B* **27**, 1413 (1983).
- [11] G. Bergmann, *Physics Reports-Review Section of Physics Letters* **107**, 1 (1984).
- [12] G. Bergmann, *Zeitschrift Fur Physik B-Condensed Matter* **48**, 5 (1982).
- [6] Y. Fehr, S. May-tal, and R. Rosenbaum, *Physical Review B* **33**, 6631 (1986).
- [14] Although the original paper by Maekawa and Fukuyama [9] includes the Zeeman splitting term γ that is proportional to the electron g-factor and external magnetic field H , the magnetic field we use in our experiments is small enough to ignore this term.
- [15] T. Koga, J. Nitta, T. Akazaki, and H. Takayanagi, *Physical Review Letters* **89**, 046801 (2002).
- [16] A. D. Caviglia, M. Gabay, S. Gariglio, N. Reyren, C. Cancellieri, and J. M. Triscone, *Physical Review Letters* **104**, 126803 (2010).
- [17] This is only true up to the first order scatterings [4]. We assume that the second and higher order spin-flip processes are negligible.
- [18] B. L. Altshuler, A. G. Aronov, and D. E. Khmelnitsky, *Journal of Physics C-Solid State Physics* **15**, 7367 (1982).
- [19] The measured proportionality constant, which according to the theory [18] depends on sheet resistance, is actually larger by a factor of 7 than what the theory predicts. Although we do not understand the reason of this disagreement, similar discrepancy between theory and experiment has been reported in the literature [32]. We also note that, if we calculate the proportionality constant at 4.5 K for the Cu film of [12] and scale it with the sheet resistance, the result agrees with our value.
- [20] Since the antiferromagnetic propagation vector of CuO is along the (101) direction [33], we assume that the spins in the (111) surface of our film do not order ferromagnetically.
- [21] M. A. Ruderman and C. Kittel, *Physical Review* **96**, 99 (1954).
- [22] T. Kasuya, *Progress of Theoretical Physics* **16**, 45 (1956).
- [23] K. Yosida, *Physical Review* **106**, 893 (1957).
- [24] Strictly speaking, this may not be genuine spin glass in the sense that the relaxation time is infinite, because the spin glass should not occur in a two-dimensional system from a theoretical point of view. Even so, the relaxation time can be long enough to exhibit a hysteresis in our experimental time scale.
- [25] A. Sherman and N. Voropajeva, *International Journal of Modern Physics B* **24**, 979 (2010).
- [26] M. Snoek, I. Titvinidze, C. Toke, K. Byczuk, and W. Hofstetter, *New Journal of Physics* **10**, 093008 (2008).
- [27] A. Gozar, G. Logvenov, L. F. Kourkoutis, A. T. Bollinger, L. A. Giannuzzi, D. A. Muller, and I. Bozovic, *Nature* **455**, 782 (2008).
- [28] O. Yuli, I. Asulin, O. Millo, D. Orgad, L. Iomin, and G. Koren, *Physical Review Letters* **101**, 057005 (2008).
- [29] V. J. Emery, S. A. Kivelson, and O. Zachar, *Physical Review B* **56**, 6120 (1997).
- [30] E. Berg, D. Orgad, and S. A. Kivelson, *Physical Review B* **78**, 094509 (2008).
- [4] P. Phillips, *Advanced Solid State Physics* (Westview Press, Boulder, 2003).
- [32] M. E. Gershenson, *Annalen Der Physik* **8**, 559 (1999).
- [33] M. Ain, A. Menelle, B. M. Wanklyn, and E. F. Bertaut, *Journal of Physics Condensed Matter* **4**, 5327 (1992).

TABLE II. Summary of the SIMS measurement in ppm.

^{51}V	^{52}Cr	^{55}Mn	^{56}Fe	^{58}Ni	^{59}Co	^{102}Ru
0	0.1	1	2	2	4	0

SYNTHESIS AND CHARACTERIZATIONS OF FILMS

Our copper monoxide (CuO) film was synthesized on a magnesium oxide (001) substrate by electron-beam evaporation in a vacuum chamber with the base pressure at least better than 1×10^{-8} torr. In order to prepare smooth and clean substrate before deposition, an ultrasonically cleaned MgO (001) substrate was annealed first at 500°C in vacuum for a few hours and further at 750°C under RF-excited atomic oxygen flux [1] for 10 minutes. A few nanometers of homoepitaxial MgO was then deposited by pulsed laser deposition using a Mg target at 750°C under the atomic oxygen flux, which yielded a very smooth and chemically clean MgO surface. Following the cleaning procedure, the substrate was cooled down to 500°C, where Cu was deposited using the electron beam evaporation under the atomic oxygen to synthesize a 21 nm CuO film.

X-ray diffraction study has shown that the (111) direction of our CuO film is aligned parallel to the (001) direction of the MgO substrate, in the similar manner to the works in the literature [2]. Although the CuO film is not single crystalline due to the twinning of CuO with respect to MgO, the (111) peak of the x-ray diffraction is sharp with the FWHM of the rocking curve smaller than 0.2° , suggesting a good crystalline quality. In addition, the atomic force microscope measurement has shown that the RMS roughness of the surface is only about 0.5 nm, which makes it possible to synthesize a ultrathin continuous Cu film on top of the CuO.

We also looked for trace magnetic impurities in a 300 nm-thick Cu film deposited from the same Cu source by using a secondary ion mass spectrometry (SIMS) [3]. Table II shows that Cr, Mn, Fe, Ni, and Co were found out of the 7 elements investigated. The total concentration of these magnetic elements is ~ 10 ppm. We note that the measured concentration is accurate only up to a factor of ~ 2 , due to our rough estimate of sensitivity factors.

INTERPRETATIONS OF TRANSPORT DATA

When one observes a minimum of sheet resistance in a thin metallic film, there are at least 3 possible explanations for the minimum: the weak localization/antilocalization, the Kondo effect [4], or the electron-electron interaction in a disordered system [5]. It is therefore sometimes difficult to determine which one is significant. In our study, however, we believe that our

magnetoconductance analysis focusing only on the weak localization/antilocalization is valid at least above 2 K from the following reasons.

If the Kondo effect played a major role in our data, the magnetoconductance would not depend strongly on the direction of the applied magnetic field. Moreover, the minimum of resistivity due to the Kondo effect would occur at the same temperature regardless of the thickness of the film. Neither turned out to be true for our films.

As for the effect of electron-electron interactions, it is probable that, as shown by [6], the temperature dependence of sheet resistance in Fig. 1 does include a significant contribution from this effect. However, it does not affect the results of our analysis using the low-field magnetoconductance.

Finally, the result in Fig. 3 that shows temperature-independence of H_1 strongly implies that our analysis is valid without taking either the Kondo effect or the electron-electron interaction into account.

ORIGIN OF MAGNETIC IMPURITIES

Even though we found the trace magnetic impurities in our Cu source by the SIMS measurement, it may not be a sufficient proof that they are the only source of the spin-flip scattering. In particular, it is known [6] that oxidation of Cu by moisture in air does occur and can affect the transport properties. We could therefore imagine that oxygen atoms cause the spin-flip scattering as well. The latter interpretation is consistent with the observation that the effective thickness we noted in the Table I is much smaller than the nominal thickness, probably due to the oxidation of the surface of the films.

We actually attempted to prevent the oxidation of our Cu samples by depositing an additional capping layer. However, the choice of the best material for the capping layer turned out to be difficult. The first material we tested was Al_2O_3 , but we found that it reduced the reproducibility of sheet resistance, probably because of the oxidation of Cu during the growth of the capping layer. We also deposited Si as the capping layer, but it was found that Si layer deposited at room temperatures could easily conduct current and confuse the interpretation of the data.

We however emphasize that, since H_1 is correctly estimated to be temperature-independent, our analysis of the magnetoconductance by utilizing the weak antilocalization formula seems valid, regardless of the oxidation of our samples. In addition, our main conclusion is independent of the source of spin-flip scatterings, because it relies only on the comparison between the Cu/CuO and the Cu/BI films.

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- [1] N. J. C. Ingle, R. H. Hammond, M. R. Beasley, and D. H. A. Blank, *Applied Physics Letters* **75**, 4162 (1999).
- [2] I. M. Watson, M. P. Atwood, and T. J. Cumberbatch, *Thin Solid Films* **251**, 51 (1994).
- [3] NanoSIMS 50L by CAMECA, SAS.
- [4] P. Phillips, *Advanced Solid State Physics* (Westview Press, Boulder, 2003).
- [5] P. A. Lee, and T. V. Ramakrishnan, *Review of Modern Physics* **57**, 287 (1985).
- [6] Y. Fehr, S. May-tal, and R. Rosenbaum, *Physical Review B* **33**, 6631 (1986).